

Oscillator Strengths for $B - X$, $C - X$, and $E - X$ Transitions in Carbon Monoxide

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Received _____; accepted _____

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ABSTRACT

Band oscillator strengths for electronic transitions in CO were obtained at the Synchrotron Radiation Center of the University of Wisconsin-Madison. Our focus was on transitions that are observed in interstellar spectra with the *Far Ultraviolet Spectroscopic Explorer*; these transitions are also important in studies of selective isotope photodissociation where fractionation among isotopomers can occur. Absorption from the ground state ($X\ ^1\Sigma^+ v'' = 0$) to $A\ ^1\Pi (v' = 5)$, $B\ ^1\Sigma^+ (v' = 0, 1)$, $C\ ^1\Sigma^+ (v' = 0, 1)$, and $E\ ^1\Pi (v' = 0)$ was measured. Fits to the $A - X$ (5, 0) band, whose oscillator strength is well known, yielded the necessary column density and excitation temperature. These parameters were used in a least-squares fit of the observed profiles for the transitions of interest to extract their band oscillator strengths. Our oscillator strengths are in excellent agreement with results from recent experiments using a variety of techniques. This agreement provides the basis for a self-consistent set of f -values at far ultraviolet wavelengths for studies of interstellar (and stellar) CO.

Subject headings: ISM: molecules – molecular data – ultraviolet:ISM

1. Introduction

Carbon monoxide, the second most abundant interstellar molecule, is seen in cloud envelopes through absorption at ultraviolet wavelengths. At wavelengths above 1200 Å, spectra acquired with the *Hubble Space Telescope* (*HST*) revealed CO absorption from the dipole allowed $A - X$ series of bands (Sheffer et al. 1992; Lambert et al. 1994; Lyu, Smith, & Bruhweiler 1994) and from several weak triplet-singlet bands (Federman et al. 1994). At shorter wavelengths, the (0, 0) bands of the allowed $B - X$, $C - X$, and $E - X$ transitions were seen in spectra taken with the *Copernicus* satellite (e.g., Morton 1975; Snow 1975; Federman et al. 1980). The recently launched *Far Ultraviolet Spectroscopic Explorer* provides the means to study these short-wavelength transitions again.

Oscillator strengths are required to convert the observed amount of absorption into abundances or column densities. Recent experimental work, using a variety of techniques, has produced a set of self-consistent f -values for the bands at 1200 Å and beyond. In particular, the results of Chan et al. (1993), Smith et al. (1994), Federman et al. (1997), Jolly et al. (1997), Zhong et al. (1997), Stark et al. (1998), and Eidelsberg et al. (1999) for $A - X$ ($v' = 5-16$) agree within experimental uncertainties, typically 10%. As for the triplet-singlet bands, the analysis of Rostas et al. (2000) confirms the f -values inferred from *HST* observations by Federman et al. (1994). The accuracy of these f -values now is also 10%.

The situation for transitions involving the Rydberg states, B , C , and E , where factor-of-2 differences persist, is less satisfactory. The results of earlier experiments based on CO absorption (Eidelsberg et al. 1991; Stark et al. 1992) tended to be smaller than those f -values obtained in electron-energy-loss and electron-impact-excitation experiments (Chan et al. 1993; Kanik et al. 1995; Ciocca et al. 1997; Zhong et al. 1997). Theoretical determinations (Kirby & Cooper 1989; Chantranupong et al. 1992; Rocha, Borges, & Bielschowsky 1998) usually favored the smaller values, but spanned a factor-of-2 range. In this paper, we present new results based on absorption of synchrotron radiation. Our f -values are consistent with the results of experiments using electrons and with the recent work of Stark et al. (1999) on $B - X$ (0, 0) and (1, 0), which

involved absorption of laser light. The combined effect is that interstellar studies now have a reliable set of CO f -values covering the range 1050 to 1550 Å.

These results impact other facets of CO spectroscopy. First, the destruction of CO in interstellar space and circumstellar envelopes involves line absorption into predissociating levels (e.g., Bally & Langer 1982; van Dishoeck & Black 1988; Warin, Benayoun, & Viala 1996). All states lying above the E ($v = 1$) state predissociate. Absorption into the E ($v = 0, 1$) and C ($v = 1$) states leads to photodissociation a significant fraction of the time. The photodissociation rate depends on the optical depth of the absorption line, which in turn depends on the line oscillator strength. Use of larger f -values, as suggested by our work and others, will alter model predictions. Second, once oscillator strengths are known, measurements of the branching fraction for transitions to the ground state reveal upper state lifetimes (e.g., Cacciani et al. 1998). We obtained lifetimes from our f -values and available branching fractions and compared these with information in the literature.

2. Experiment

Our absorption experiment was conducted at the Synchrotron Radiation Center of the University of Wisconsin-Madison. The setup is shown in Figure 1. Ultraviolet (UV) light was collimated through the entrance slit of the 4 m Normal Incidence Monochromator and passed through a LiF window before entering a CO gas cell that is 14.6 cm long. At the end of the gas cell, the UV light was converted into visible light by a sodium salicylate coating on a flange window. The light was focused by a lens onto the cathode of the photomultiplier tube (PMT) (Hamamatsu R3788). The photocurrent from the PMT was converted into voltage and sampled by an analog-to-digital converter. The beam current from the synchrotron and the total pressure inside the gas cell were continuously monitored. A Pirani ion gauge was used for pressures above 1.3 mTorr, and a cold cathode ionization gauge was used for lower pressures. Slit widths of 15 and 20 μm were used to maximize the spectral resolution, yielding $\delta\lambda$ of ~ 0.11 Å. The total gas pressure ranged from 0.3 to 18.3 mTorr, corresponding to CO column densities of 8×10^{13}

to $5 \times 10^{15} \text{ cm}^{-2}$, values that are observed in interstellar clouds. In the analysis that follows, we used column densities derived from synthesized spectra of measurements on the $A - X$ (5, 0) band instead of pressures to minimize systematic effects arising from impurities contributing to the pressure and from measurements with two pressure gauges. Data were acquired on $B - X$ (0, 0), $B - X$ (1, 0), $C - X$ (0, 0), $C - X$ (1, 0), and $E - X$ (0, 0) bands. Wavelength scans at every band for each pressure in the cell were followed by a scan at $A - X$ (5, 0) at the same pressure. The data for the $A - X$ (5, 0) band were used to place our results for the Rydberg bands on an absolute scale. In most instances several scans were obtained for a specific pressure. The step size was set either to 0.01 or 0.02 Å for a scan; no systematic effects on the derived f -values were noticed for scans with different step sizes.

The transmission curve of the system is given in Figure 2, with the CO bands superposed. In addition to the bands analyzed here, several other features are present in Fig. 2. First, there is a contaminant, most likely water, with features between 1200 and 1250 Å and near 1125 Å. While the latter occurs where the $B - X$ (1, 0) band lies, it is sufficiently broad that no problems arose in extracting the band of interest. At the higher pressures, the $B - X$ (2, 0) and $E - X$ (1, 0) bands were seen. The $B - X$ (2, 0) band was always too weak to derive a reliable f -value from the data. Since an accurate measurement of the $A - X$ (5, 0) band was necessary, the pressure could not be set arbitrarily high to get good data on $B - X$ (2, 0). While the signal to noise was better for the $E - X$ (1, 0) band, no reliable determinations were possible because this band lies too close to the LiF cutoff.

3. Analysis and Results

The data for each band was processed in much the same way as in Federman et al. (1997). The dark current from the PMT, which was measured before each scan by closing a mechanical shutter to the beamline, was subtracted from the signal and the beam current drift was removed by normalizing to the beam current curve for the scan. The data were corrected for the transmission curve of the setup, which was obtained with no CO in the cell. Spectra taken at a given pressure

were combined. The flux from the synchrotron was fit to a low order polynomial, yielding normalized spectra for each pressure. In some instances, a Gaussian fit to the contaminant feature near the $B - X$ (1, 0) band was needed to aid in its removal. The latter 3 steps utilized the NOAO/IRAF package.

The next steps involved the spectra of the $A - X$ (5, 0) band. Each normalized spectrum was synthesized with a least-squares fitting routine (cf. Lambert et al. 1994) used by us in our earlier CO experiment (Federman et al. 1997). In essence, the routine minimizes the difference between measured and synthesized amounts of absorption. The synthetic spectrum was based on line wavelengths from Tilford & Simmons (1972) and the well-determined f -value of 1.45×10^{-2} (e.g., Chan et al. 1993). Voigt line profiles were adopted for all syntheses. Excitation temperature, wavelength offset, column density, and instrumental width (well approximated by a Gaussian) were varied. Once the instrumental width for each of the two slit-widths (~ 0.11 Å) was determined, the spectra were resynthesized, giving the column density for a specific pressure. This column density was used in the fit of the Rydberg bands. As in our earlier work, the excitation temperature was usually less than room temperature. This difference arises because the high-lying rotational levels decay radiatively at the pressures in the gas cell. We investigated the effects of changing the excitation temperature on the derived f -values for the Rydberg bands; the f -values changed by 1% or less. For excitation temperatures in the range 250 to 300 K, the absorption was spread over many rotational levels, thereby reducing the effect of optical depth on individual lines.

The determination of the f -values for Rydberg bands at various pressures was accomplished through profile synthesis, varying only the wavelength offset and f -value. Here the line lists of Eidelsberg et al. (1991) were used because they were the most complete. The wavelengths for the $B - X$, $C - X$, $E - X$ bands studied by us were not affected by the recalibration described in Eidelsberg et al. (1992). The initial f -values in the fitting process were those listed by Morton & Noreau (1994). Typical fitting results for each band are presented in Figure 3. For the strong $C - X$ (0, 0) band, the data for a pressure of 0.6 mTorr are shown; all other fits are to data taken at 3 mTorr.

The uncertainty in the inferred oscillator strengths includes a statistical component and a systematic one. The statistical error in the f -value for a band at a specific pressure was obtained by summing in quadrature the error in the equivalent width (W_λ) of the reference band, the error in W_λ of the band in question, and the error in the reference band f -value, taken to be 5% (Chan et al. 1993). A conservative uncertainty in W_λ was determined by multiplying the root-mean-square variation in the continuum flux from the synchrotron by the width of the profile at half-maximum depth. Systematic effects included variations in pressure for a given set of measurements ($\leq 5\%$), uncertainties in instrumental width ($\leq 5\%$) and in excitation temperature ($\leq 1\%$), and the problems fitting the Q branch for $E - X$ (0, 0) ($\leq 5\%$), as noted in the next section. The combined effect introduces a maximum uncertainty of 8.7% in our derived oscillator strength for the $E - X$ (0, 0) band and 7.1% in the others.

The experimental results for each absorption band are summarized in Table 1. The error bars quoted there are due to statistics only. Results are only shown for pressures where the signal to noise in the continuum allowed a meaningful determination and where problems associated with optically thick lines were kept to a minimum. The excellent agreement in derived f -value from one pressure to another gives us confidence in the results. At the largest pressures for a given band, the optical depth at line center for the strongest line in the $B - X$ and $C - X$ bands is modest (≤ 6). While the optical depth for the Q(7) line of the $E - X$ (0, 0) transition reaches nearly 40, the results are consistent for all pressures with optical depths from 0.9 to ~ 40 . A comparison of our results with other experimental and theoretical results is presented in Table 2. Here the uncertainty includes systematic errors as well.

4. Discussion

4.1. Fits to Rydberg Bands

Several comments about the fits to the Rydberg bands (Fig. 3) deserve mention. In all cases, fits to the P and R branches show less absorption for the high-lying rotational levels than is

observed. Changes in excitation temperature do not remedy the situation. A more likely cause lies in the fact that our fits are restricted to lines for levels up to $J = 25$. While Tilford & Simmons (1972) included more levels in their compilation, their list for the Q branch of the $E - X$ (0, 0) band was incomplete. We felt that self-consistency in use of line list was more important than the slight deviations in profile synthesis for lines involving high-lying rotational levels in the P and R branches. Moreover, the fraction of CO molecules in $J \geq 26$ at an excitation temperature of ~ 280 K is less than 0.2%; absorption from these levels contributes less than about 1% to the total W_λ for a band. Such a small effect was not considered in the error budget.

Our fit to the Q branch of $E - X$ (0, 0) is less than satisfactory because the fit suggests more absorption than is seen in the laboratory data. Eidelsberg et al.’s (1991) line list for the Q branch is based mainly on theoretical estimates because the band was not resolved. Recent laser experiments (Cacciani, Hogervorst, & Ubachs 1995) indicate that the rotational constant for the e -parity Λ -doublet component (Q branch) is about 0.5% larger than the one for the f component (P and R branches). This translates into a broadening of the Q branch, which would allow syntheses to track the measured profiles better. Since Cacciani et al. did not give a line list, we preferred to use the available information in Eidelsberg et al. (1991). The measured wavelengths for the P and R lines in Eidelsberg et al. are consistent with other determinations; typical differences of 3 mÅ with Tilford & Simmons (1972), for instance, are seen. (Since our synthesis is based on all three branches, the resulting f -value for the band is not likely to be affected greatly. A systematic uncertainty of at most 5% applies to the effect noted here.)

4.2. Oscillator Strengths

Our results are in excellent agreement with the recent work of Ciocca et al. (1997), Zhong et al. (1997), and Stark et al. (1999). Good agreement with Chan et al. (1993) and Kanik et al. (1995) is also seen. For the (0, 0) bands, earlier absorption work by Eidelsberg et al. (1991) and Stark et al. (1992) gave significantly smaller f -values, but results of Eidelsberg et al. show consistency with the recent work for the relatively weak (1, 0) bands. A systematic trend is seen

in the results presented by Eidelsberg et al.: The discrepancy between their f -values and the more recent determinations increases with increasing band strength. This trend suggests optical depth effects were not adequately treated in their analysis of CO absorption. The results of Stark et al. (1992) may be affected by this problem as well. Agreement with theoretical results is seen at the factor-of-2 level. Rocha et al. (1998) showed that the differences between their theoretical oscillator strengths, those of Chantranupong et al. (1992), and the experimental ones of Zhong et al. (1997) mainly arise from the differences in Generalized Oscillator Strength (GOS) for small K^2 , the square of the transferred momentum. The fact that all experimental techniques now give oscillator strengths similar to the ones obtained by Zhong et al. indicates more theoretical work on the GOS at small K^2 is warranted.

The results presented here and from other recent experiments impact the models of CO photodissociation. According to the models of van Dishoeck & Black (1988), the $E - X$ (0, 0) band plays an important role. Their modeling efforts are based on the oscillator strengths of Letzelter et al. (1987), later updated by Eidelsberg et al. (1991). The recent experiments, including ours, indicate the f -values of Eidelsberg et al. for the strongest bands are too small, by nearly a factor of 2 for the $E - X$ (0, 0) band. The discrepancy appears for f -values greater than about 6×10^{-3} . All other bands found to be important in the photodissociation process by van Dishoeck & Black have f -values greater than 7.5×10^{-3} , according to Letzelter et al. (1987). We suspect that all these f -values have to be revised upward. Such a revision would greatly influence model predictions. In particular, lines become optically thick closer to a cloud’s edge when f -values are larger. The effect would be enhanced self-shielding of the most abundant isotopic variant, $^{12}\text{C}^{16}\text{O}$, leading to enhanced fractionation relative to other isotopomers. Such an effect could explain the large column ratios, $N(^{12}\text{C}^{16}\text{O})/N(^{13}\text{C}^{16}\text{O})$, seen toward ζ Oph (Lambert et al. 1994). For the $E - X$ (0, 0) band, which has a substantial radiative decay channel, the photodissociation yield is somewhat lower as well (see Cacciani et al. 1998).

4.3. Radiative Lifetimes

With a self-consistent set of oscillator strengths for the Rydberg bands now available, radiative lifetimes for the upper state can be inferred from branching fractions for transitions to the ground electronic state. The relationship between band oscillator strength, branching fraction, and lifetime is given in Morton & Noreau (1994):

$$(2 - \delta_{0\Lambda''}) f_{v'v''} = 1.499 \times 10^4 (2 - \delta_{0\Lambda'}) \lambda_{v'v''}^2 A_{v'v''}, \quad (1)$$

where λ is the wavelength of the transition in meters and $A_{v'v''}$ is the transition probability in s^{-1} . The branching fraction γ and radiative lifetime $\tau_{v'}$ are related by

$$\gamma = A_{v'v''} / \sum_{v''} A_{v'v''} = A_{v'v''} \tau_{v'} \quad (2)$$

with the lifetime in seconds. For the X , B , and C states, $\delta_{0\Lambda}$ is 1. Combining these facts leads to the expression

$$f_{v'v''} = 1.499 \times 10^4 \lambda_{v'v''}^2 \gamma / \tau_{v'} \quad (3)$$

from which we can derive $\tau_{v'}$, knowing γ .

We focus on the $B - X$ (0, 0) and $C - X$ (0, 0) transitions, which do not lead to absorption into predissociating levels. Essentially all decays from the upper states B and C ($v' = 0$) return the molecule either to the X or A states (Letzelter et al. 1987; Kirby & Cooper 1989), with nearly all decays to ground involving $v'' = 0$. Experimental $B - X$ branching fractions span the range 0.56 to 0.68 (Dotchin, Chubb, & Pegg 1973; Letzelter et al. 1987; Drabbels, Meerts, & ter Meulen 1993), indicating respective lifetimes of 17 to 20 ns when using our f -value. The early measurements, summarized by Krishnakumar & Srivastava (1986), and those of Drabbels et al. (1993) yielded lifetimes that are too long by 1 to several standard deviations. The measurements

of Hart & Bourne (1989) are the most consistent with available branching fractions and our f -values. The corresponding $C - X$ branching fractions range from 0.94 to 0.99 (Dotchin et al. 1973; Letzelter et al. 1987; Drabbels et al. 1993), leading to a lifetime of ~ 1.4 ns for the C ($v' = 0$) state. Again, many of the measurements indicate lifetimes that are 1- to 2- σ too long, but the results of Hesser (1968) and Chornay, King, & Buckman (1984) are consistent with our inferred lifetimes. The lifetime of Drabbels et al. is much too short. The fact that many of the lifetime determinations are too long suggests radiative trapping may have adversely affected the results. As for the $E - X$ (0, 0) transitions, Cacciani et al. (1998) provide a similar analysis; their results using the f -value of Chan et al. (1993) appear to be the most appropriate.

5. Final Remarks

New results for oscillator strengths of several Rydberg bands in CO were obtained from an absorption experiment using synchrotron radiation. The results are in excellent agreement with other recent experimental determinations based on laser absorption, electron energy loss, and electron impact excitation. These independent measures reveal that a self-consistent set of band f -values for the $B - X$ (0, 0) and (1, 0), $C - X$ (0, 0) and (1, 0), and $E - X$ (0, 0) transitions is now available for studies of interstellar (and stellar) CO. Such studies include observations with the *Far Ultraviolet Spectroscopic Explorer* and models of CO photodissociation. The f -values for the strongest transitions are larger than once thought. Theoretical models of interstellar chemistry using the new f -values will show more fractionation of $^{12}\text{C}^{16}\text{O}$ relative to less abundant forms. Finally, combining available branching fractions for transitions between the upper and ground states with our f -values provided the means to obtain radiative lifetimes for the upper states. For the B and C states with $v' = 0$, shorter lifetimes are most consistent with the set of larger f -values.

We thank Yaron Sheffer for the code used in profile synthesis. The research was supported by NASA grants NAG5-4957, NAG5-6729, and NAG5-7754 to the University of Toledo and by NSF grant DMR-95-31009 to the Synchrotron Radiation Center.

Table 1
Experimental Results

Pressure (mTorr)	f -values ($\times 10^3$)				
	$B - X$ (0, 0)	$B - X$ (1, 0)	$C - X$ (0, 0)	$C - X$ (1, 0)	$E - X$ (0, 0)
0.3	123 ± 10	...	66 ± 6
0.6	122 ± 11	...	60 ± 6
1.0	61 ± 4
1.29	74 ± 4
1.65	7.1 ± 0.5	0.76 ± 0.35	...	3.1 ± 0.6	69 ± 4
3.01	6.7 ± 0.5	0.79 ± 0.18	...	2.9 ± 0.6	63 ± 4
6.08	...	1.09 ± 0.42
6.09	5.7 ± 0.6	0.70 ± 0.41	...	2.6 ± 1.0	72 ± 5
6.78	6.7 ± 0.5	69 ± 4
9.03	...	0.79 ± 0.37
9.75	6.9 ± 0.4	0.68 ± 0.15	...	3.1 ± 0.4	70 ± 4
12.1	...	0.92 ± 0.22
12.5	6.4 ± 0.6	0.92 ± 0.27	...	3.0 ± 0.6	68 ± 5
12.9	6.4 ± 0.5	0.96 ± 0.22	...	2.7 ± 0.5	75 ± 5
18.1	6.7 ± 0.5	0.70 ± 0.14
18.3	6.9 ± 0.5	0.89 ± 0.18
average	6.7 ± 0.2	0.80 ± 0.06	123 ± 7	3.0 ± 0.2	68 ± 1

Table 2
Comparison of Results

Reference	f -values ($\times 10^3$)				
	$B - X$ (0, 0)	$B - X$ (1, 0)	$C - X$ (0, 0)	$C - X$ (1, 0)	$E - X$ (0, 0)
Experiment:					
Present results ^a	6.7 ± 0.7	0.80 ± 0.12	123 ± 16	3.0 ± 0.4	68 ± 7
Lassettre & Skerbele 1971 ^b	15 ± 3	2.0 ± 0.4	163 ± 15	7.0 ± 0.6	94 ± 9
Eidelsberg et al. 1991 ^a	4.52 ± 0.45	0.72 ± 0.07	61.9 ± 6.2	2.77 ± 0.28	36.5 ± 3.7
Stark et al. 1992 ^a	49.0 ± 5.0
Chan et al. 1993 ^b	8.03	1.32	117.7	3.56	70.6
Kanik et al. 1995 ^c	12 ± 3	...	154 ± 41
Ciocca et al. 1997 ^c	70.8 ± 18.4
Zhong et al. 1997 ^b	5.98 ± 0.93	...	114 ± 14	3.22 ± 0.94	64.2 ± 8.1
Stark et al. 1999 ^d	6.5 ± 0.6	1.1 ± 0.1
Theory:					
Kirby & Cooper 1989	2.1	0.3	118.1	1.8	49
Chantranupong et al. 1992	5.08	0.52	64.7	4.9	27.4
Rocha et al. 1998	4.8	0.43	89	2.9	49

^a Synchrotron absorption.

^b Electron energy loss.

^c Electron impact excitation.

^d Laser absorption.

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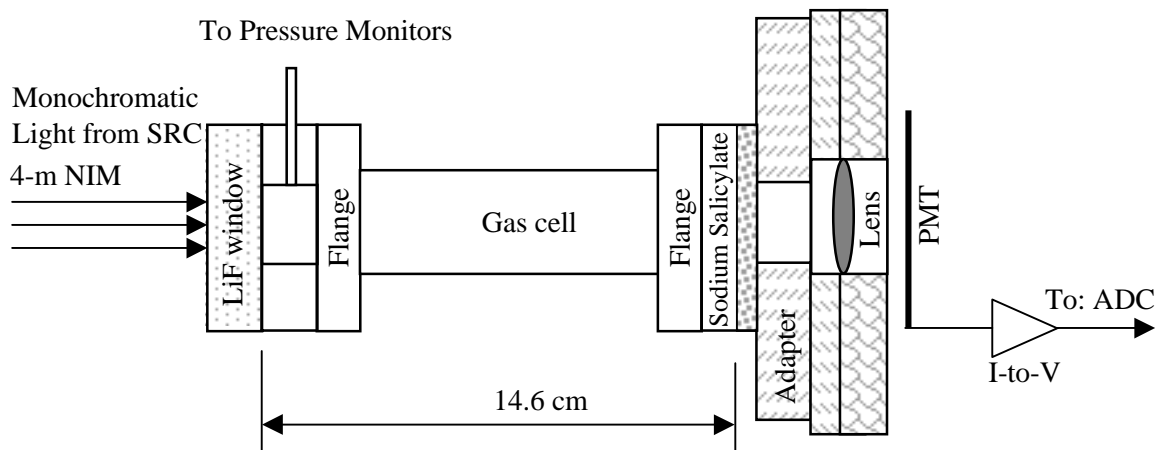


Fig. 1 – A schematic of the experimental setup at the 4 m Normal Incidence Monochromator beamline used for the CO measurements.

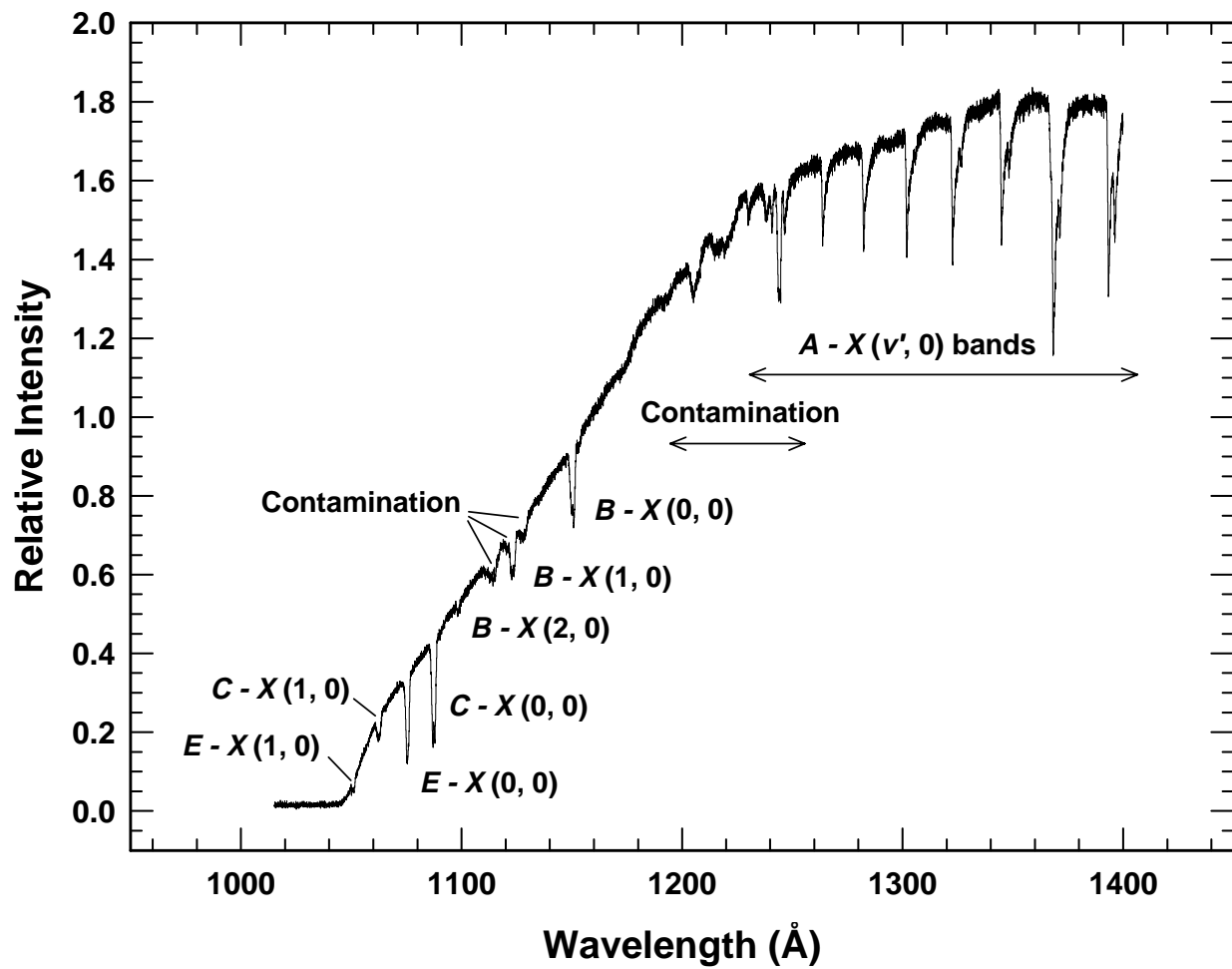


Fig. 2 – A scan showing the transmission curve of the LiF windows with a superposed spectrum of CO. The CO bands are indicated, as are features from a contaminant, most likely H_2O .

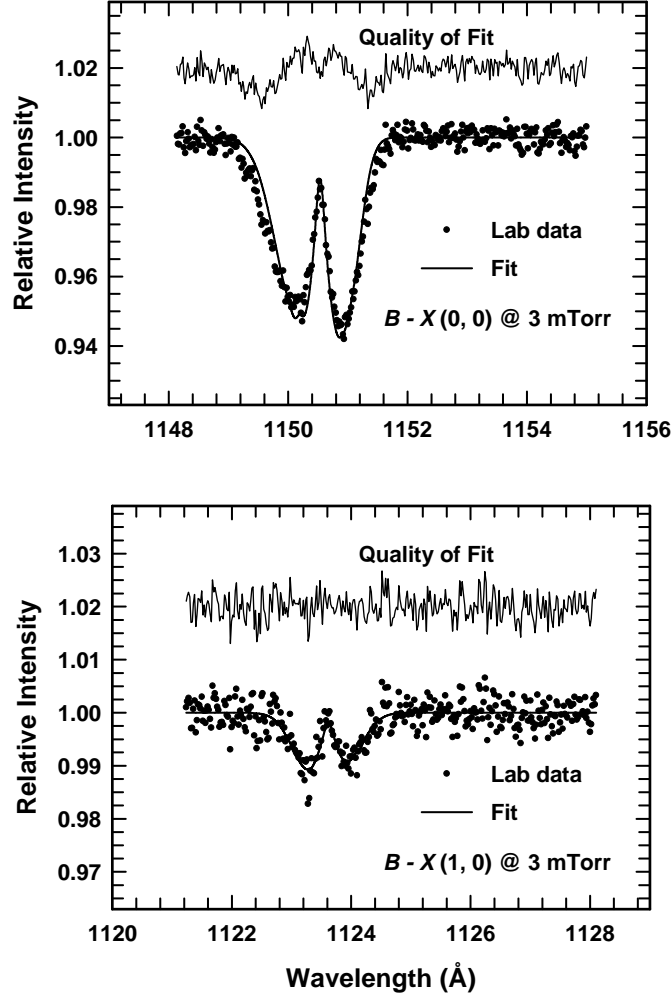


Fig. 3 – Fits to the CO bands. a) $B - X$ (0, 0) and (1, 0) bands. b) $C - X$ (0, 0) and (1, 0) bands. c) $E - X$ (0, 0) and $A - X$ (5, 0) bands. The strong $C - X$ (0, 0) band was taken at a pressure of 0.6 mTorr; all other data are from a pressure of 3 mTorr. The data are represented by filled circles, the syntheses by thick curves, and the quality of the fit by thin lines. The quality of the fit indicates the difference between fit and data, offset to 1.02. The spectrum for the $C - X$ (1, 0) band has lower signal to noise, the result of lying near the LiF cutoff; here the quality of the fit is offset to 1.03.

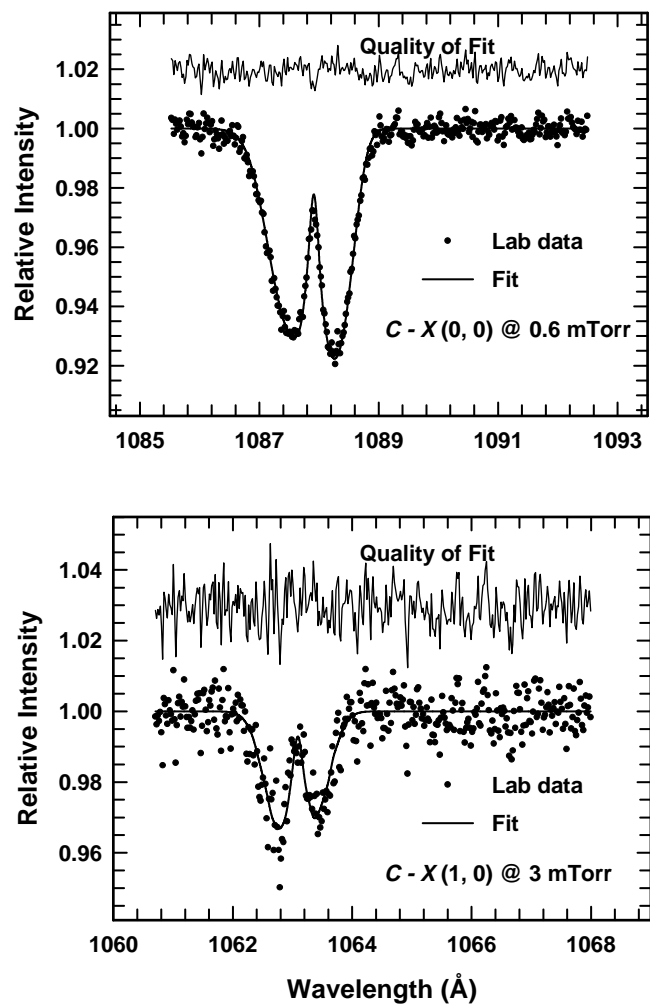


Fig. 3b

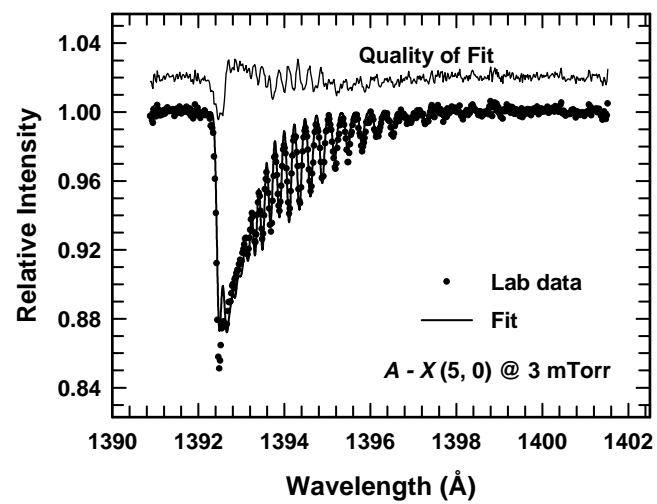
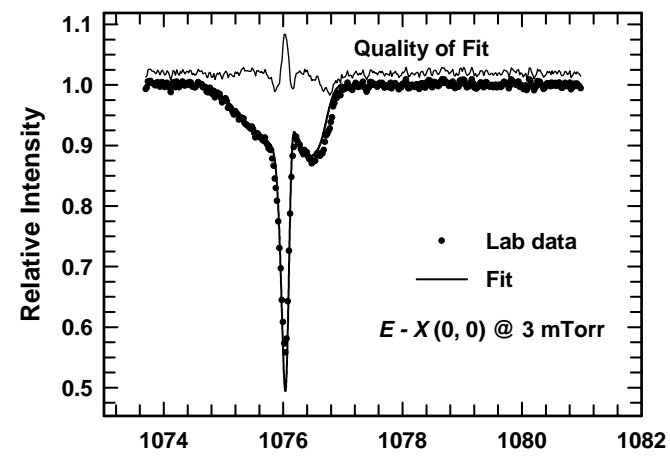


Fig. 3c